Photoresponse of Plasma Sprayed TiO₂-Rutile Semiconductor†

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Abstract

Plasma spraying has been used to prepare n-type polycrystalline TiO₂ coatings on titanium. Photoelecrero-chemical properties of the plasma sprayed TiO₂ (rutile) coating photoanodes were measured in oxygen-saturated aqueous solution of 0.1N NaOH. The photoresponse of plasma sprayed TiO₂ coatings have been studied and compared with air oxdized films of titanium.

The photoresponse of the plasma sprayed TiO₂ coating photoanodes to band and subband gap energies were explored as a function of wavelength and intensity of monochromatic light, applied potential and adititive in coatings.

The photoresponse was shown to increase linearly with light intensity, and to depend on the square root of applied potential.

These results suggest a bulk photoexcitation process involving impurity and defect levels in the energy gap of semiconductor plasma sprayed TiO₂ (rutile) coatings. A qualitative model was presented to account for the main features of this exitation process.

KEY WORDS: (Photoresponse) (Plasma Spraying) (TiO₂), (Rutile) (Semiconductor)

1. Introduction

Plasma spraying is a well known technique used in aeronautic applications to obtain the durable coatings of metals, alloys and ceramics. Our study was to see if good quality polycrystalline TiO₂ coatings are easily obtained by plasma spraying, the TiO₂ coatings are important for application in solar energy and the elctronics industries.

When rutile titanium dioxide is treated to be oxygen defficient, the material becomes a n-type semiconductor whose property depends on the extent of oxygen loss.

The loss of oxygen in TiO₂ lattices can be achieved by either heating in a low oxygen pressure or in hydrogen atmosphere (1−2). By these processes TiO₂ is turned into non-stoichiometric TiO_{2-x} and Ti_nO_{2n-1} known as the magneli series of homogeneous compounds.

An industrial coating technique, plasma spraying, has been used to produce TiO₂ polycrystalline coatings from TiO₂ powders on titanium or alumina substrate. Other investigations reported that photoresponse of the plasma sprayed TiO₂ anodes behave similarly to other polycrystalline TiO₂ electrodes made by other technique (3-5). But photorespone of TiO₂ coatings depends greatly on plasma spray condition, adititve and heat treatment (5). In this study, the photoresponse of plasma sprayed TiO₂ (rutile) coatings were studied, compared with air oxidized films of titanium. A model is presented which describes this excitation process and explains the dependence of the photoresponse on the wavelength and intensity of the light.

2. Materials and Experimental Procedure

The materials used in this investigation was commercially available TiO₂ powder with composition rutile TiO₂: bal., Al_2O_3:1.03, SiO_2:0.08, Fe_2O_3:0.07, CaO:0.13, MgO:0.05, Na_2O:0.04 wt%, with particle size 10−44μm. Y_2O_3 powder with purity 99.99wt% was used as additive. The substrate was titanium plate with purity 99.84 wt%, size 25mm × 15mm × 3mm.

First, the TiO₂ photanodes were prepared by plasma spraying. Plasma spraying was performed with a METCO 7M plasma spray system. Plasma spraying was done in air atmosphere with a plasma gas of Ar (100 1/min) and H₂ (10 1/min). Plasma power was 38kW and spraying distances were 100 mm. In this experiment a additive of 0 to 1 % Y₂O₃ was used. After plasma spraying, plasma sprayed
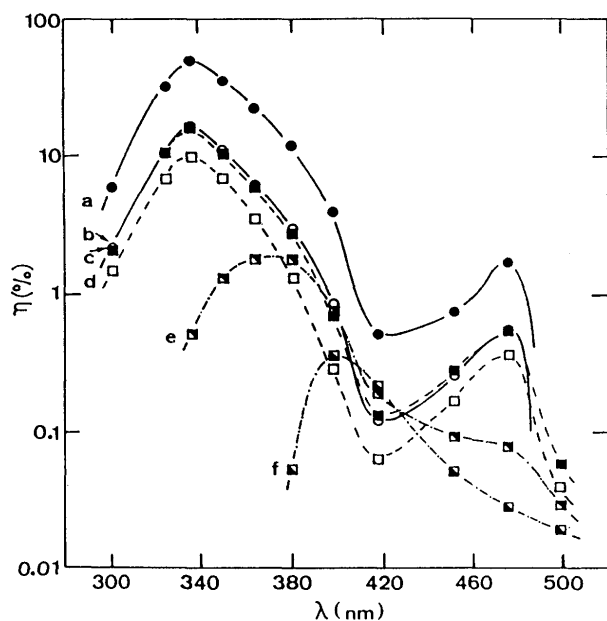
coatings were heat-treated at 400°C for 90 minutes.

Secondly, the titanium oxide films that titanium plates were oxidized in air were prepared as photoanodes. The samples were always introduced in the electrical furnace under air atmosphere at the temperature of the treatment, and they were cooled slowly in furnace.

In order to perform photoresponse measurements on the photoanodes, ohmic contacts were made by attaching a copper wire to the conducting titanium substrate. All the nonphotoactive parts of the photoelectrode were afterwards covered with silicone rubber to avoid photoresponse, leaving an active area of 1 cm².

The photoelectrochemical measurements were performed in a three electrode cell equiped with a quartz window, using a 0.1N NaOH electrolyte saturated with oxygen at atmosphere. The counterelectrode was Pt foil, and the reference was a standard calomel elctrode.

The working electrode was illuminated with white light from a high pressure 300W Xe lamp. Monochromatic light for quantum yield determination was obtained by use of an interference filter. The light intensity was measured by an Epply Thermopile, type E6. Photocurrent measurments were performed with a potentiostat and function generator.

(a)TiO₂-1%Y₂O₃ coating
(b)TiO₂ coating
(c)Oxidized Ti plate(600°C)
(d)Oxidized Ti plate(400°C)
(e)Oxidized Ti plate(800°C)
(f)Oxidized Ti plate(1000°C)

Fig. 1 Spectral dependence of the photoefficiency (η) for various electrodes (plasma sprayed TiO₂-1%Y₂O₃ (a) and TiO₂ (b) coatings, and oxidized Ti-plate (heat-treatment: 600°C-90 min. (e) and 1000°C-1 min. (f)

All the measurements were performed at room temperature.

3. Results and Discussion

We define the photocurrent (P_c) in this paper as the current difference between the constant dark current and the constant illumination current (6). When the monochromatic light of 300—700nm was illuminated into the electrodes-electrolyte interface, the photoefficient peaks were observed at 340 and 476nm, as shown in **Fig. 1**. The photefficiency-peak of subband wavelength (476nm) are in agreement with -2.60eV (476nm) position of the trap level (7) and defect-related gap state (8) of TiO₂ (rutile) were reported previously. The photocurrent efficiency (η) was calculted from $\eta = p_c/qI_o$, where I_o is the photon flux absorbed by the electrode surface in contact with the electroyte. The expermental errors of the photocurrent efficiency can be estimated to be ±5% and probably due to inacccurate measurement.

The plasma sprayed TiO₂ and TiO₂−1%Y₂O₃ coating electrodes were made using hydrogen flow of 10 1/min in air, and then were heat-treated at 400°C for 90 minutes in air. As a result, two remarkable features of the spectral dependences are brought about by plasma spraying. One is the appearance of peak of the photoresponse due to the LW (long wavelength) lights. The other is the peak due to the SW (short wavelength) lights. The appearances of the response peak for the TiO₂ plasma sprayed electrodes in this experiment were alike. But, the photoefficiencies of TiO₂ plasma sprayed electrodes due to the SW lights (for band gap response) and the LW light (for subband gap response) increased by adding 1%Y₂O₃.

The oxidized titanium electrodes were made in heat-treatment conditions, such as 400°C-90 min, 600°C-90 min, 800°C-10 min, 1000°C-1 min in air. Two remarkable features of the spectral dependence of these electrodes are brought by the heat-treatment. The peak of the photoefficiencey due to the SW lights becomes sharp and shifts to the longer wavelength with the increase of heat-treatment temperature. Moreover, no peak of photoresponse to the LW lights is observed at heat-treatment of 1000°C.

And, almost the same spectral dependences were obtained for both the plasma sprayed TiO₂ coating electrode and the oxidized titanium electrode that heat-treated at 600°C in air.

The important clue to the nature of the band gap and subband gap photoresponse comes from the relation between the applied potential and photocurrent.

Analysis of the response of the Schottky junction at the semiconductor-electroyte interface has shown that the photocurrent density (P_c due to illumination may be ex-
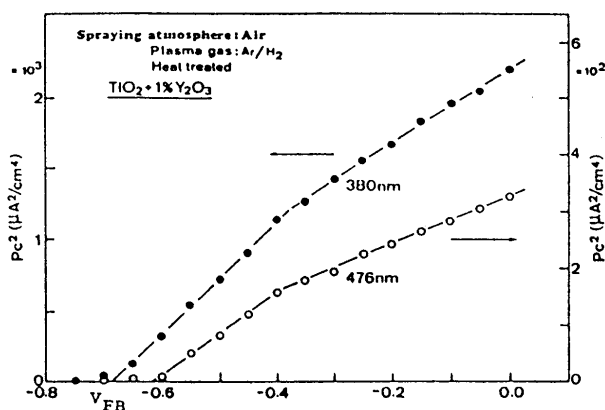
Fig. 2 Square of photocurrent versus applied potential of plasma sprayed TiO₂-1%Y₂O₃ coatings.
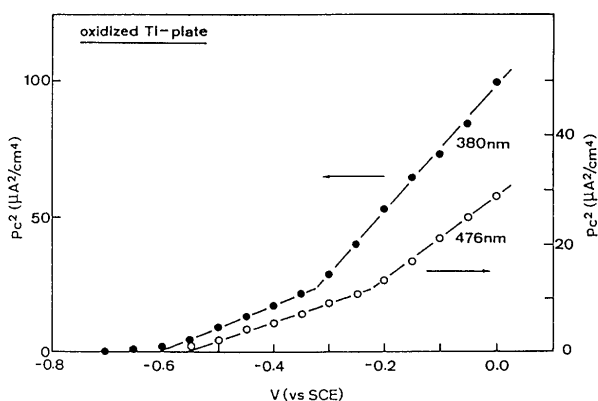

Fig. 3 Square of photocurrent versus applied potential of oxidized Ti-plate heat-treated at 600°C during 90 min.

pressed (9) as $P_c^2 = (qI_0\alpha W_0)^2$ (V-V$_{FB}$), where, V is the applied potential at the photoanode, I_0 is the photon flux absorbed by the electrode surface in contact with electrolyte, V$_{FB}$ is the flat-band potential of the photoanode, q is the charge of an electron, α is the optical absorption efficient, W_0 is a constant depending on the properties of the semiconductor. Under the assumptions that $\alpha w \ll 1$, $\alpha L p$ $\ll 1$, and no electron-hole recombination, the above corelation between the photocurrent and the applied potential can be obtained for the process. Also, $W(=W_0 \,(V\text{-}V_{FB})^{1/2})$ is the depletion layer thickness and L_p is the minority carrier diffusion length.

At 380nm and 476nm wavelengths, **Fig. 2** and **Fig. 3** show the relation P_c^2 and applied potential V for plasma sprayed TiO₂-1%Y₂O₃ coatings and the oxidized titanium that heat-treated at 600°C, respectively. These figures show that the square of the photocurrent depends linearly on potential and extrapolates to zero at the flatband potential. Where the double tunneling or double excitation process can be reasonable neglected since it generally results in very small photocurrents (10).

Since a bulk process occures uniformly throughout the depletion layer region, the observed band and subband gap

photresponse is bulk phenomenon occurring throughout the depletion layer. For surface state exitation square root dependence on applied potential would not expected (10—11). Different slopes of these figures may represent nonuniform or a change of donor concentration as a function of distance. (12)

We obtained flat band potentials of 380nm and 476nm wavelength at 298K, for plasma sprayed TiO₂-1% Y₂O₃ coatings, they were 0.685V, 0.620V (versus SCE), respectively and for the oxidized film of heat-treated titanimum at 600°C, they were 0.625V, 0.560V respectively.

These flat band potentials of plasma sprayed TiO₂-Y₂O₃ coatings were larger than that of the oxidised film. But, the differences of flat band potentials for the 380nm and 476nm wavelenght were kept constant, 0.065V. And, These flat band potentials were smaller than the typical value (0.8~1.0V) for n-TiO₂ in 1N NaOH(13—14).

The bandgap (E$_g$) for the plasma sprayed TiO₂-1%Y₂O₃ coatings obtained from the plots $(\eta h\nu)^{1/2}$ vs hν, as shown in **Fig. 4**, was 2.93 eV, this is lower than typical value (3.05) for TiO₂ (15—16). The plots in this figure are based on the relation,

$$\eta h\nu = [L_p + W_0(V - V_{FB})^{1/2}] \; A \; (h\nu - Eg)^{1/2} \text{ given by}$$

Butler(9), assuming the validity of the Schottky barrier theory for these semiconductor-electrolyte junctions. Where, A is constant and hν is light intensity. The decrease of E$_g$ as well as the positive shift of V$_{FB}$, could resonably be related to a tailing of the band gap absorption due to energy states near the band-edges. These states are verly likely associated with Ti-O bonds whose convalency is weakended in the disordered lattice (17—18). And plasma
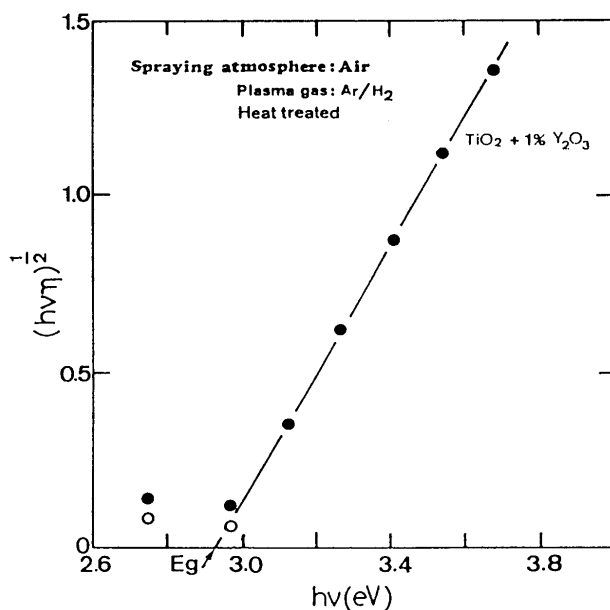

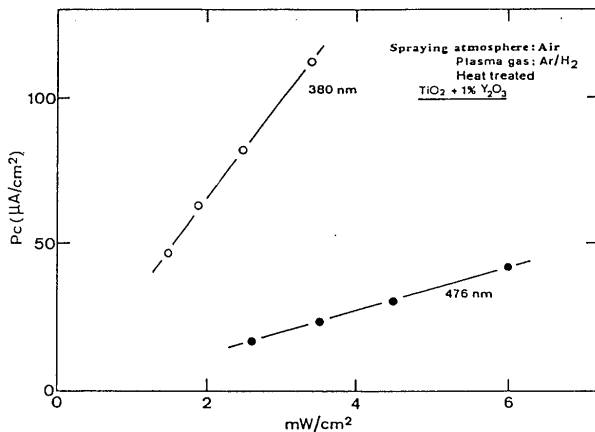**Fig. 4** Determination of E$_g$ from the variation of (h$\nu\eta$)$^{1/2}$ as a function of hν

Fig. 5 The incident light intensity versus band and subband gap photocurrent for plasma sprayed TiO₂-1%Y₂O₃ coatings.

Fig. 7 Energy band diagram of plasma sprayed TiO₂ coatings-electrolyte system.

sprayed TiO_2 and oxidized titanium films should have many trap levels because of the oxygen vacancies from nonstoichiometric defects. These trap levels might have the same optical properties as the trap levels of TiO_2 single crystal. Therefore the photoresponse of the subband gap should appear.

The dependence of the phototoresponse for plasma sprayed TiO_2-1%Y_2O_3 coating electrode on wavelength and intensity of light is the linear relationship as shown in Fig. 5. These results agree with the suggestion by Rose (19). Having the photocurrent proportional to the light intensity suggests the presence of traps which possibly have a uniform distribution in the forbidden gap in the neighborhood of the Fermi level or are concentrated below the Fermi level. Thus we believe that the excitation mechanism is a native defect in the bulk. And, these are impurities and defect levels.

TiO_2 (rutile) is the tetragonal structure. Each Ti^{+4} ion is coordinated by an oxygen octahedron that is distorted to orthorhombic symmetry (20) The valance band is the Ti-Oπ band and the conduction band is the Ti-Oπ^* band. The π and π^* bands are formed by the interaction between the t_{2g} orbital of the Ti cation and the P_π orbital of the oxygen ion. The band strucure of the TiO_2 (rutile) is
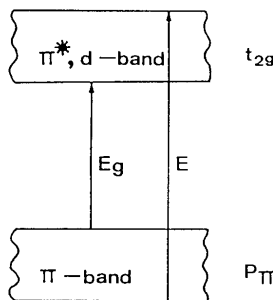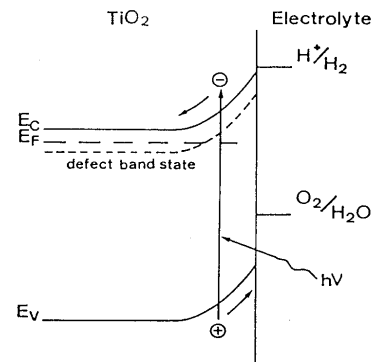

Fig. 6 Band structure of TiO_2.

shown in Fig. 6 (21−22).

Since the hole is formed in the band by the π band-π^* band transition, the photocurrent appears only when the lights with the wavelengths corresponding to the energies from E_g to E are illuminated. When a $h\nu$ photon falls on TiO_2 of bulk of the TiO_2 coatings (or films), the photochemical reaction will result in the creation of the pair: electron e^--hole$^+$.

The broadness and the position of the peak of the photoefficiency due to the SW lights in oxidized titanium of figure 1 will be mainly determined by the degree of the interaction between the t_{2g} orbital of Ti cation and the P_π orbital of the oxygen ion, which will depend on the distance between both ions (14). If the interact ion becomes weak, the peak of the photocurrent becomes sharp and shifts to the long wavelength, ie., the low energy transition.

If a form of defects formed by the plasma spraying is same in the plasma sprayed coatings, the shapes of the phtoefficiency vs wavelength-graph are same. But the values of the photoefficiency should be different by the degree of reduction and trapping of impurity into defect bands.

Observed subband gap response is a bulk phenomenon occurring throughout the depletion layer as shown in figure 2 and figure 3. Therefore, subband gap response probably involves the model of bulk photoexcitation processes as shown in Fig. 7.

The photoresponse to the LW lights should be observed at these electrodes because the electrons may be photoexcited from the valance band to the empty (Ti: 3d $[t_{2g}]$) sub levels from where they tunnel to the conduction band (23). The energy difference between the conduction band and the Fermi level in TiO_2 is about 0.2eV (14), and photoefficiency-peak of 476nm wavelength in this work agreed with the defect levels with mainly Ti-3d contribution 0.3eV(9) below the conduction band edge, this gap state is formed by line defect with missing rows of oxygen.

And, if the impurity was trapped at defect site, the TiO_2-defect band due to the impurity should be formed a

little below the π^* conduction band in energy position.

4. Conclusions

The results of this paper clearly show that band and subband gap excitation of semiconducting plasma sprayed TiO_2 photoelectrodes are possible by a bulk mechanism, and proposed that the relevant subband gap states arise from charge compensating effects of defects generated by the impurity doping process. And the photocurrents of additional $1\%Y_2O_3$ plasma sprayed coatings are very large compared to nonadded coating and the oxidized titanium.

The trapped electrons are excited to the conduction band of the TiO_2 coatings by the absorption of monochromatic light, and the repeated circuration of this process generates continuous flow of the photocurrent. The generation mechanism of photoresponse in this band and subband gap region explains that the photocurrent depends linearly on the intensity of illuminated light.

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